Ratios of Methylmercury to Total Mercury in Predator and Primary Consumer Insects from Adirondack Streams in New York State

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Ratios of Methylmercury to Total Mercury in Predator and Primary Consumer Insects from Adirondack Streams in New York State

Summary Report

Prepared for:

New York State Energy Research and Development Authority

Albany, NY

Diane Bertok,
Project Manager

Prepared by:

United States Geological Survey

Troy, NY

K. Riva-Murray
Project Manager

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Abstract

Mercury (Hg) is a global pollutant that affects aquatic biota in otherwise pristine settings such as the Adirondack region of New York State. Bioaccumulation of Hg is especially problematic in sensitive landscapes, where inorganic mercury from atmospheric deposition is readily converted, via natural processes, to methylmercury (MeHg), the toxic form that is taken up and biomagnified in aquatic food webs. There is great interest in monitoring MeHg in aquatic biota across these sensitive regions to evaluate responses to changes in Hg emissions. Aquatic insects, such as dragonfly larvae, have great potential as MeHg "biosentinels," but currently are not widely used for this purpose. An important practical consideration in the use of aquatic insects for MeHg biomonitoring is whether total mercury (THg) is a suitable surrogate for MeHg, which is much more technically challenging and expensive to analyze than is THg. The objective of this project was to assess the suitability of THg as a surrogate for MeHg in stream-dwelling insects. Specifically, existing data on immature aquatic insects from nine Adirondack streams were used to characterize MeHg to THg ratios (i.e., MeHg%), and variation in these ratios (e.g., among sites, seasons, taxa) in predator and primary consumer insects, examine how well THg in different groups tracks measured stream water MeHg (i.e., filtered MeHg; FMeHg), and explore the influence of trophic position (indicated by nitrogen stable isotopes; $\delta^{15}N$) on the observed MeHg% patterns.

Three broad insect feeding groups were included in this analysis: predators, shredders, and scrapers. Predators had the highest MeHg% (median 94%), and MeHg% did not differ significantly among any of the taxa considered: stoneflies, damselflies, and three families of dragonflies (darners, common skimmers, and clubtails). Darners and common skimmers, the most numerous and abundant predators, were combined for further analyses. Site medians for these "selected dragonflies" were all at least 90% (summer-fall collections) and MeHg% did not differ significantly among sites. The correlation between FMeHg and THg in selected dragonflies was nearly as strong as that of FMeHg and dragonfly MeHg. In contrast, median MeHg% in shredders (northern caddisflies) and scrapers (flathead mayflies), which are both primary consumers, was lower overall (medians 52% and 35%, respectively), more variable, and less-well representative of FMeHg than predators. Stable isotope results indicate that variation in feeding position is an important influence on some of the MeHg% patterns observed in this study. This study's findings suggest that THg is likely to be a suitable surrogate for MeHg in predatory aquatic insects from Adirondack streams, but do not support the use of THg in primary consumers for regional MeHg monitoring.

Keywords

bioaccumulation, aquatic insects, methylmercury, total mercury, mercury ratios, dragonfly, northern caddisfly, flathead mayfly, streams, Adirondack region

Acknowledgments

This research was supported by funds from the New York State Energy Research and Development Authority under the direction of Diane Bertok, and the United States Geological Survey (USGS). The USGS National Water Quality Assessment Program funded the original collection and laboratory analysis of macroinvertebrate samples, which provided all data used in this research. The authors greatly appreciate the advice and insight provided by John De Wild (USGS, Wisconsin Mercury Research Laboratory), Daniel Button (USGS, Ohio Water Science Center), and Barbara Eikenberry (USGS, Wisconsin Water Science Center). Any use of trade, firm, or product names in the report is for descriptive purposes only and does not imply endorsement by the U.S. government. For more information on the ratios of methylmercury to total mercury in macroinvertebrates from Adirondack streams, summarized in this report, please see the full article in *Ecotoxicology*. The full citation for this article is: Riva-Murray, K., P.M. Bradley, and M.E. Brigham (2020), Methylmercury - total mercury ratios in predator and primary consumer insects from Adirondack streams (New York, USA).[1]

[1] *Ecotoxicology,* https://doi.org/10.1007/s10646-020-02191-7

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1 Focus

Existing aquatic insect MeHg and THg concentration data from a 2007–2009 United States Geological Survey (USGS) National Water Quality Assessment Project study of Adirondack streams in New York State were analyzed to describe how the ratio of MeHg to THg (i.e., MeHg%) varies across taxa, feeding groups, stream sites, and seasons. Stable isotope data ($\delta^{15}N$) from that study were also used to determine the extent to which observed patterns of MeHg% are related to trophic position, and MeHg data from filtered stream water samples (i.e., FMeHg) were used to examine how well THg in aquatic insects can represent the observed FMeHg patterns. Three broad feeding groups were considered: predators, shredders, and scrapers (the latter two generally considered primary consumers). Predators consisted of dragonflies (Odonata) in three families (Aeshnidae [darners], Libellulidae [common skimmers], and Gomphidae [clubtails]); damselflies (Odonata: Zygoptera); and stoneflies (Plecoptera). Shredders were all northern caddisflies (Trichoptera: Limnephilidae) and scrapers were all flathead mayflies (Ephemeroptera: Heptageniidae).

Figure 1. Collection and Field Processing of Insect Samples, and Collection of Stream Water Samples

Shown (from left to right) are photos of aquatic insect sample collection, field-processing of aquatic insect samples, and collection of a stream water sample for mercury analysis.

Source photo credit Dennis Wentz, USGS

2 Context

Methylmercury (MeHg) is a potent neurotoxin that readily enters the base of aquatic food webs, where it can bioconcentrate and biomagnify to concentrations that can be harmful to humans, fish-eating wildlife, and fish themselves. Biomonitoring of MeHg, to evaluate responses to recent changes in mercury air emissions and atmospheric deposition, is of great interest in northeastern North America. Aquatic insects and other aquatic macroinvertebrates possess qualities that are desirable as MeHg biosentinels. For example, they are important in MeHg transfer from primary producers (such as algae) to fish, and in the transfer of aquatic MeHg to terrestrial food webs. Many insect taxa are broadly distributed (including in fish-less habitats), locally abundant, relatively easy to collect and identify, and live in aquatic habitats for a year or more. An important practical consideration in the use of aquatic insects for MeHg biomonitoring is whether THg is a suitable surrogate for MeHg, which is much more technically challenging and expensive to analyze than is THg. Because the percentage of THg comprised of MeHg in aquatic insects can exhibit large and unknown taxonomic, spatial, and temporal variation, an evaluation of the suitability of THg as a MeHg surrogate in particular groups is warranted. Furthermore, achieving a greater understanding of the factors underlying variation in MeHg% among feeding groups, taxa, sites, and seasons can advance the design of MeHg monitoring with aquatic insects.

Figure 2. Photos of Representative Immature Aquatic Insects in Primary Consumer and Predator Feeding Groups

Shown (clockwise from upper left) are photos of the immature, aquatic, life stage of a scraper (flathead mayfly, Ephemeroptera: Heptageniidae), predator (common skimmer dragonfly, Odonata: Libelluidae) and shredder (northern caddisfly, Trichoptera: Limnephilidae).

Source photo credit Mark Brigham.

3 Goals and Objectives

The goal of this study was to provide a tool for the effective use of aquatic insects in Hg monitoring. Specific objectives were to (1) document ratios of MeHg to THg (i.e., MeHg%) in predators and primary consumer aquatic insects from Adirondack streams, (2) describe the extent of taxonomic, seasonal, and site-to-site variation in MeHg% of these groups, (3) determine if the observed variation in MeHg% is related to trophic position (as indicated by nitrogen stable isotope data), and (4) evaluate whether or not biotic THg tracks patterns of MeHg in filtered water (FMeHg) as well as MeHg in each feeding group.

4 Study Area and Methods

The Adirondack region of New York State receives relatively high amounts of atmospheric mercury, is remote from mercury point sources, has wetlands and soil characteristics that are conducive to methylation of deposited mercury, and has fish mercury concentrations that are elevated in relation to human and wildlife health thresholds and guidelines. Nine study sites were located in the upper Hudson River Basin in the central part of the Adirondack region (Figure 3). These consisted of eight sites in the Fishing Brook watershed (65.6 km^2 drainage area) and one site on the upper Hudson River (493 km^2 drainage area).

Insect MeHg and THg concentration data, stable isotope data ($\delta^{15}N$), and stream water FMeHg data were compiled from the National Water Information System.[2] The δ15N is an indicator of trophic position; higher values generally represent higher food chain positions, and base-adjusted values ($\delta^{15}N_{adj}$) are used for comparisons among sites. Insect data were from 260 composite samples of immature aquatic insects collected May to October in 2007–2009. Samples were collected throughout each stream reach by hand-picking, kick-netting, and/or bank jabbing with nets. The FMeHg data were from a single water sample per site and visit collected during non-storm conditions, generally within several days of insect sample collection. All samples were collected and field-processed with trace-metal clean methods. Data from 2007 and 2008 were used for comparisons among sites, because only two sites were sampled during 2009. Prior to the calculation of MeHg%, a recovery-based correction was applied to THg concentration data derived from a direct combustion laboratory method to remove the effect of laboratory method (whether direct combustion or cold-vapor atomic fluorescence spectroscopy) on the results.

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2 National Water Information System USGS Water Resources, http://dx.doi.org/10.5066/F7P55KJN

Figure 3. Study Area Map

Streams from which macroinvertebrate and water samples were collected during 2007–2009 as part of the mercury cycling and bioaccumulation study of the USGS National Water Quality Assessment Project. Data from these samples were used in the current study. Site abbreviations correspond with site names provided in Table 1.

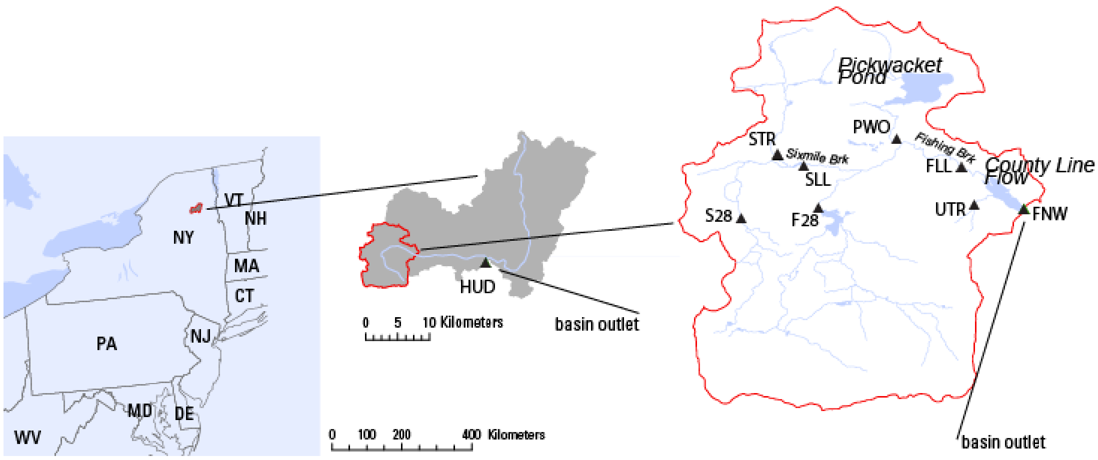


Table 1. Site List

List of sites in the Adirondack region (New York State) from which insects were collected and analyzed for total mercury and methylmercury as part of the USGS National Water Quality Assessment Project during 2007–2009. The USGS station identifier, drainage area, and functional feeding groups (FFGs) collected from each site is shown. SC = scraper; SH = shredder; PR = predator.

Site Abbre-viation	USGS Station Identifier	Site Name	Basin Area (km^2)	FFGs Collected
F28	01311990	Fishing Brook at 28N near Long Lake, NY	27.1	SC, SH, PR
FLL	0131199040	Fishing Brook above County Line Flow near Long Lake, NY	60.6	SH, PR
FNW	0131199050	Fishing Brook (County Line Flow) near Newcomb, NY	65.6	SC, SH, PR
HUD	01312000	Hudson River near Newcomb, NY	493	SC, SH, PR
PWO	0131199035	Pickwacket Pond Outlet at mouth near Long Lake, N.Y.	8.4	SH, PR
S28	0131199010	Sixmile Brook at 28N near Long Lake, NY	4.6	SH, PR
SBT*	0131199021	Sixmile Brook below Sixmile Brook tributary near Long Lake, NY	17.0	SC, SH, PR
SLL*	0131199020	Sixmile Brook near Long Lake, NY	17.7	
STR	0131199020	Sixmile Brook tributary near Long Lake, NY	6.9	SC, SH, PR
UTR	0131199045	Unnamed tributary to County Line Flow near Long Lake, NY	0.96	SC, SH, PR

* Samples from SBT were combined into SLL for the current study.

5 Project Findings

5.1 Feeding Group Comparisons

The overall median MeHg%, based on using data pooled across all sites and seasons, was highest in predators (94%), intermediate in shredders (52%), and lowest in scrapers (35%). Differences among feeding groups were large and statistically significant, both with all data combined (Figure 4) and within individual sites (Figure 5A). The higher predator MeHg% corresponded with the predator's significantly higher $\delta^{15}N$ within all five sites (Figure 5B). The extent to which THg was correlated with FMeHg varied among shredders, scrapers, and predators (selected dragonflies). The correlation of THg with FMeHg was relatively strong in selected dragonflies ($r^2 = 0.78$, $p = 0.0001$); this was similar to the correlation of dragonfly MeHg with FMeHg ($r^2 = 0.77$, $p = 0.0001$). The correlation of shredder THg with FMeHg was significant ($r^2 = 0.67$, $p = 0.0002$), but was much weaker than the observed very strong correlation of shredder MeHg with FMeHg ($r^2 = 0.83$, $p < 0.0001$). The correlation of scraper THg with FMeHg was not significant ($p = 0.84$), despite the very strong correlation of scraper MeHg with FMeHg ($r^2 = 0.85$, $p = 0.0002$).

Figure 4. Comparison of MeHg% among Feeding Groups, Over All Samples

The number of samples are indicated above x-axis. Boxes show median (horizontal solid line within box), 25th and 75th percentiles (bottom and top of box, respectively), and 10th and 90th percentiles (bottom and top horizontal lines, respectively). Dots below and above boxes are 5th and 95th percentiles, respectively. Significantly different groups are denoted by different letters above the boxes. Statistics shown are results of nonparametric analysis of variance on ranked data.

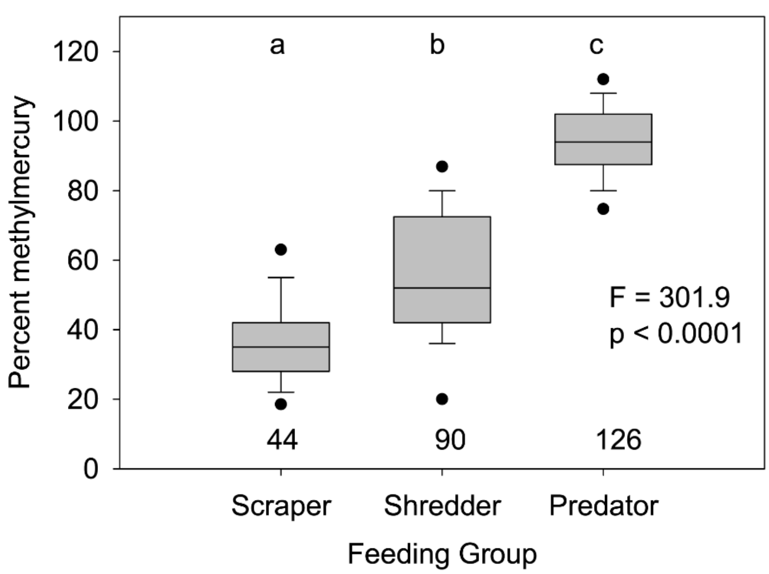
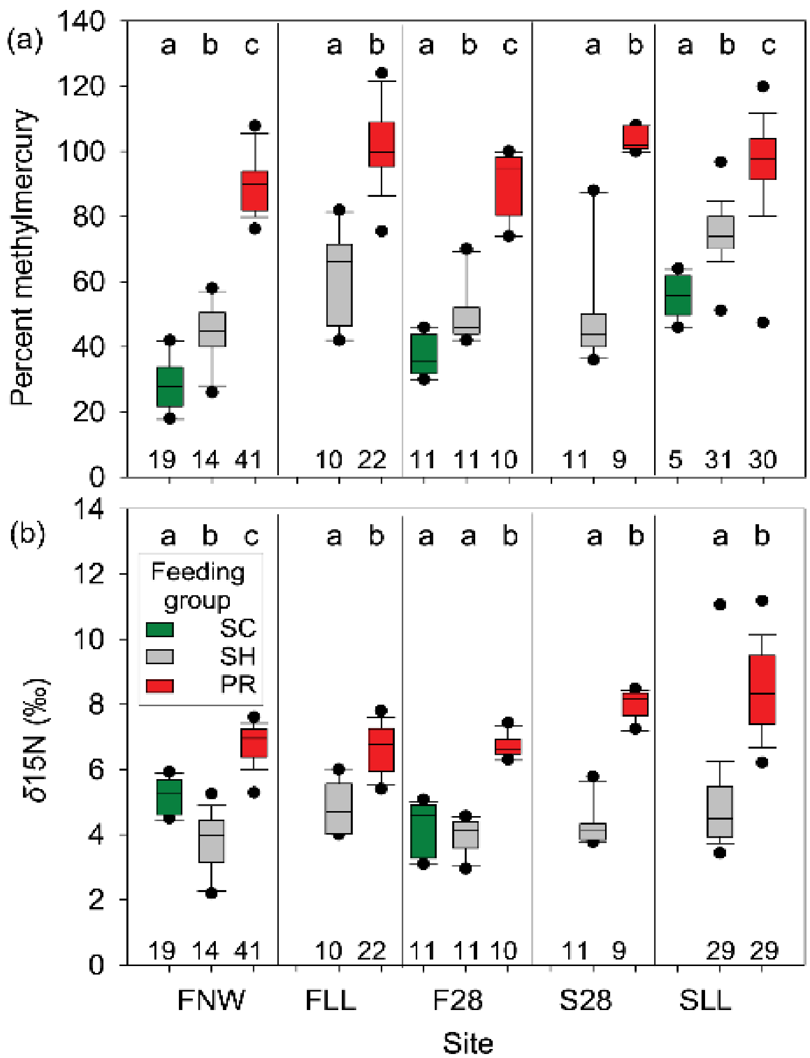


Figure 5. Comparison of MeHg% and Nitrogen Stable Isotope Values among Feeding Groups in Selected Sites

Comparison of (a) percent methylmercury (MeHg%) and (b) nitrogen isotope ratios ($\delta^{15}N$) among scrapers (SC), shredders (SH), and predators (PR) within each of the five stream sites. Selected sites have enough samples (at least five) of multiple feeding groups to compare statistically. The number of samples are indicated above x-axis. Different letters along the top denote significantly different groups within each site ($p<0.05$). Boxplot components are defined in Figure 4. Site names are provided in Table 1.



5.2 Primary Consumers

Both scrapers and shredders are generally considered primary consumers, yet site MeHg% was lower in scrapers than in shredders from the same sites (Figure 5A). This difference was statistically significant in two of the three sites considered. This is likely due to something other than trophic position, since scrapers actually had higher $\delta^{15}N$ (indicating higher trophic position) than did shredders (Figure 5B). Only one of two sites had enough samples to compare statistically.

Seasonal variation in MeHg% was apparent in both primary consumer feeding groups, with higher MeHg% values in summer than in spring (Table 2).

Large site-to-site differences in MeHg% also occurred in primary consumers within seasons during 2007–2008 (Table 2, Figure 6). Site-specific median MeHg% in scrapers ranged from 20% to 51% in spring (across four sites), from 34% to 74% in summer (across six sites), and from 39% to 64% in fall (across three sites). Shredders exhibited a very large range in median MeHg% of spring-collected samples from eight sites (from 20% to 68%; Table 2), and a statistically significant difference among the six sites with enough samples to test (Figure 6).

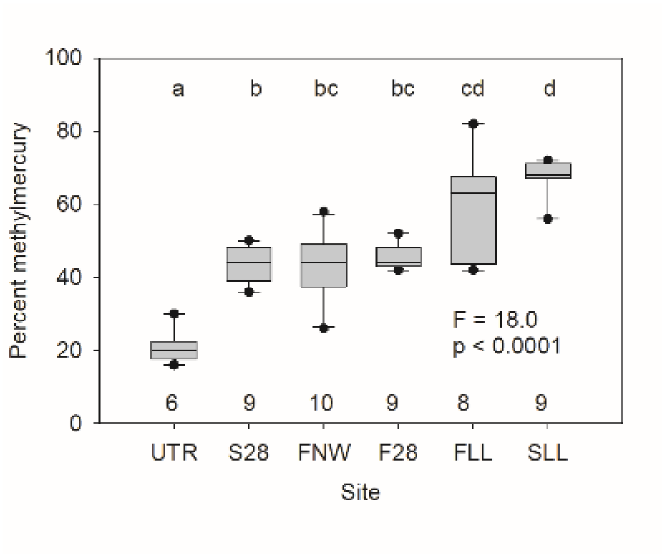
Table 2. Summary Statistics for Percent Methylmercury (MeHg%) in Shredders and Scrapers

Data are combined from samples collected during 2007 and 2008. MeHg% n = number of samples; med = median; min = minimum; max = maximum. Site abbreviations correspond with site names listed in Table 1.

Site	Season	MeHg%			
		n	med	min	max
Shredders					
F28	Spring	9	44	42	52
	Summer	2	68	66	70
FLL	Spring	8	63	42	82
	Summer	2	73	70	76
FNW	Spring	10	44	26	58
PWO	Spring	3	40	36	40
S28	Spring	9	44	36	50
	Summer	2	86	84	88
SLL	Spring	9	68	56	72
	Summer	2	98	92	104
STR	Spring	3	42	42	44
UTR	Spring	6	20	16	30
	Summer	1	92	92	92
Scrapers					
F28	Spring	6	33	30	38
	Summer	3	46	44	46
	Fall	2	39	36	42
FNW	Spring	6	22	18	30
	Summer	7	38	28	42
	Fall	3	24	22	26
HUD	Summer	4	34	28	42
SLL	Spring	2	51	46	56
	Summer	1	54	54	54
	Fall	1	64	64	64
STR	Summer	1	74	74	74
	Fall	2	43	42	44
UTR	Spring	1	20	20	20
	Summer	1	40	40	40

Figure 6. Site-to-Site Comparison of MeHg% in Shredders

Comparison of percent methylmercury (MeHg%) in shredder aquatic insects among Adirondack streams. Data are from spring-collected samples of northern case-maker caddisflies (Trichoptera: Limnephilidae) collected during 2007–2008. The number of samples are indicated above x-axis. Different letters indicate statistically significant difference. Boxplot components are defined in Figure 4. Site names are provided in Table 1. Statistics shown are results of nonparametric analysis of variance on ranked data. Sites with less than five samples are not included.



5.3 Predators

The MeHg% in predators was high, with overall medians greater than 90% in all five taxa (Table 3) and no significant differences in MeHg% among any of the taxa (Figure 7). Two dragonfly families, darners (Aeshnidae) and common skimmers (Libellulidae), were the most numerous predators and their MeHg% did not differ significantly in either of the two sites from which both were collected in large numbers. These two families of "selected dragonflies" were combined, and then each sample was classified by size as "small" or "large" (mean specimen weights < 0.06g and ≥ 0.06g, respectively). The larger (more numerous) size class was then used for site-to-site and seasonal comparisons.

The MeHg% of selected dragonflies (larger size class) did not vary significantly among seasons during 2007–2008 within the one site that had enough samples for seasonal comparisons. However, another site had significantly higher MeHg% in spring than in summer in 2009. Samples collected during spring were, thus, separated from those collected during summer and fall for the evaluation of site-to-site variation.

Median MeHg% in selected dragonflies from six sites (summer-fall collections from 2007–2008) were all at least 90% (Table 4). MeHg% did not differ significantly among the five sites with at least five samples each (Figure 8A), despite large and significant differences in $\delta^{15}N_{adj}$ (Figure 8B). This indicates that similarly high MeHg% occurs in selected dragonflies from different sites despite large differences in trophic position among sites. A greater contrast in MeHg% was observed in spring-collected samples between two sites (median MeHg% 86% and 100%, respectively; Table 4), indicating that THg might perform better as a surrogate for MeHg in the summer to fall period than in spring.

Table 3. Summary Statistics for Percent Methylmercury (MeHg%) in Predators across All Sites, Seasons, and Years (2007–2009)

MeHg% n = number of samples; med = median; min = minimum; max = maximum.

Taxon	MeHg%			
	n	med	min	max
Darner dragonflies (Odonata: Aeshnidae)	74	95	52	124
Common skimmer dragonflies (Odonata: Libellulidae)	24	93	42	112
Clubtail dragonflies (Odonata: Gomphidae)	12	95	72	124
Damselflies (Odonata: Zygoptera)	7	98	78	108
Stoneflies (Plecoptera)	9	92	78	100

Table 4. Summary Statistics for Percent Methylmercury (MeHg%) in Predators that are "Selected Dragonflies" in the "Larger" Size Class (Mean Weight $\geq$ 0.06g)

Samples were collected summer through fall during 2007–2008. MeHg% n = number of samples; med = median; min = minimum; max = maximum. Site abbreviations correspond with site names listed in Table 1.

Site Abbreviation	MeHg%			
	n	med	min	max
F28	5	96	74	100
FLL	7	102	92	116
FNW	16	94	80	108
S28	8	99	66	108
SLL	7	94	90	102
STR	2	97	96	98

Figure 7. Comparison of MeHg% among Five Taxa of Predators

The number of samples are indicated above x-axis. An absence of significant differences among groups is indicated by same letter above boxes. Boxplot components are defined in Figure 4. Statistics shown are results of nonparametric analysis of variance on ranked data.

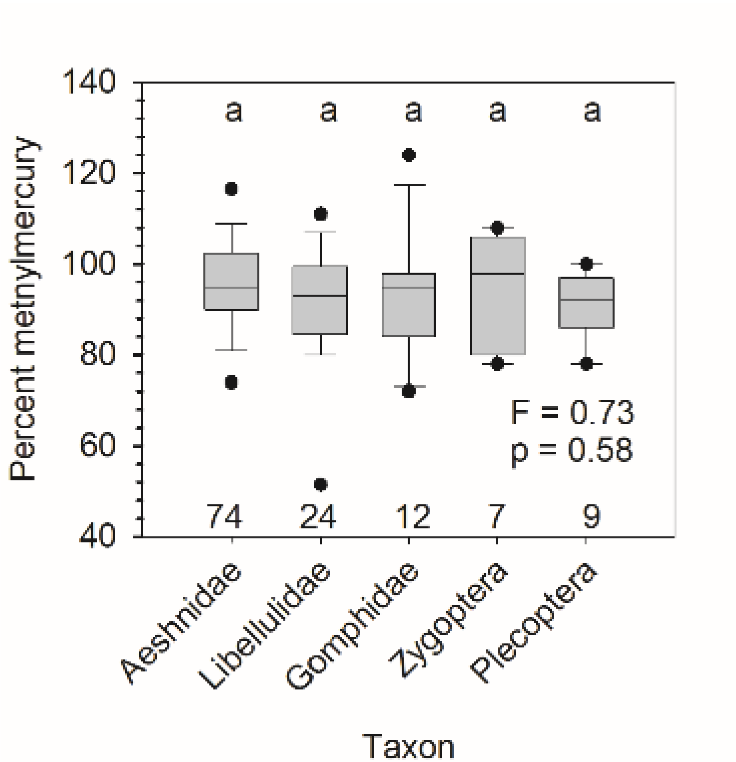
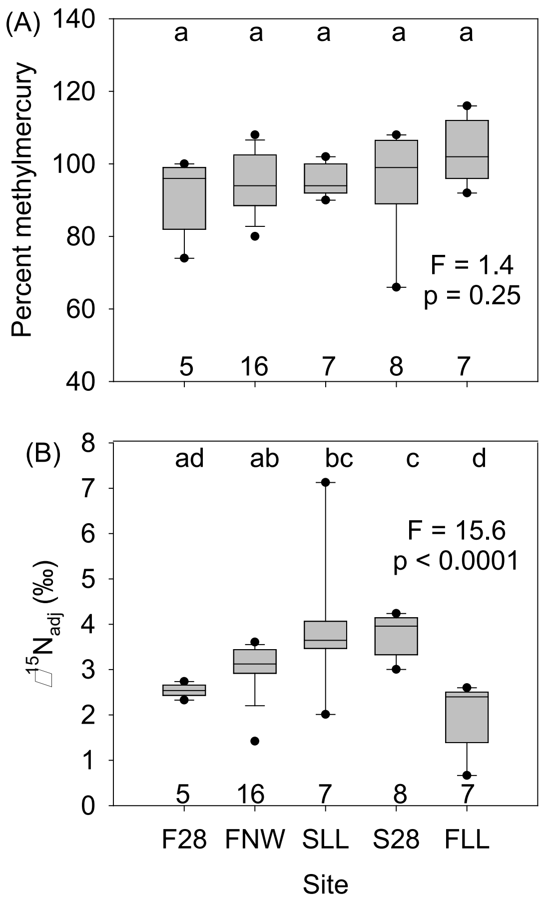


Figure 8. Site-to-site Comparison of MeHg% and Nitrogen Isotope Ratios in Selected Dragonflies

Site comparisons of (A) percent methylmercury (MeHg%) and (B) base-adjusted nitrogen isotope ratios ($\delta^{15}N_{adj}$) in selected dragonflies from Adirondack streams. Data are from summer through fall 2007–2008 collections of selected dragonflies (darner dragonflies and common skimmer dragonflies) in the larger size class. The number of samples are indicated above x-axis. Significant differences are indicated by different letters above boxes. Boxplot components are defined in Figure 4. Statistics shown are results of nonparametric analysis of variance on ranked data.



5.4 Study Implications

Predators and primary consumers in this study differed in the extent to which THg can represent MeHg concentration for biomonitoring purposes across broad areas. This is due to large differences between these two broad groups in MeHg% and in the extent of within-group taxonomic, spatial, and/or seasonal variation in MeHg%, as well as in the ability of biotic THg to track MeHg concentrations in water. These differences can be important to consider when choosing aquatic insects for MeHg biomonitoring across the Adirondacks and similar regions if there is a desire to save resources by analyzing for THg instead of MeHg.

6 Conclusions

The potential for THg to serve as a reliable surrogate for MeHg in aquatic insects varies among feeding groups and taxa. By documenting these patterns in relation to trophic position and to stream water MeHg (i.e., FMeHg) patterns, this study provides information that can help inform the best use of THg as a surrogate for MeHg in aquatic insects. Results of the current study, in a remote forested setting, indicate that MeHg comprises a relatively high percentage of the THg concentrations in aquatic insects that are obligate predators, particularly darner dragonflies and common skimmer dragonflies. Depending upon monitoring objectives and requirements, THg is more likely to be a suitable surrogate for MeHg in predatory aquatic insects than in primary consumers.

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New York State Energy Research and Development Authority

17 Columbia Circle
Albany, NY 12203-6399

toll free: 866-NYSERDA
local: 518-862-1090
fax: 518-862-1091

info@nyserda.ny.gov
nyserda.ny.gov

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